

II) Deriva. 2

DERIVATION OF  
 $P_r$  for CANONICAL  
ENSEMBLE

Lec 8 SP4  
15 (C)

Ch. 3 PHATIA

$$1) \sum_{r \neq 0} n_r E_r = \tilde{E}$$

(constraint 1)

$\tilde{E}$  = tot energy  
of  
ensemble

$$\sum_r n_r = \tilde{N}$$

(" 2)

$\tilde{N}$  = no of replicant  
systems in  
ensemble

$$W(n_r) = \frac{\tilde{N}!}{n_1! n_2! n_3! \dots}$$

[Key to whole arg.]

2) @ equil, part 2  $\Rightarrow$  maximize  $W$  subject  
to constraints:

a) let  $f(n_r) = \ln W(n_r) - \beta [\sum_r n_r E_r - \tilde{E}]$

$$- \alpha [\sum_r n_r - \tilde{N}]$$

b)  $\ln W(n_r) = \ln(\tilde{N}!) - \sum_r \ln(n_r!)$

USG  
b1) STORLING'S FORMULA:

$$\Rightarrow \ln W(n_r) = \tilde{N} \ln \tilde{N} - \tilde{N} - \sum_r n_r \ln n_r + \sum_r \frac{n_r}{\tilde{N}}$$

$$= \tilde{N} \ln \tilde{N} - \sum_r n_r \ln n_r$$

$\beta, \alpha$   
are unknown  
Lagrange  
multipliers

b2):  $f(n_r) = \tilde{N} \ln \tilde{N} - \sum_r n_r \ln n_r - \beta [\sum_r n_r E_r - \tilde{E}]$   
 $- \alpha [\sum_r n_r - \tilde{N}]$

c)  $\therefore$  @ equil:

c) constr

lec 8  
SPS 15

(2)

$$\left. \frac{\partial f}{\partial n_i} \right|_{n_i^*, n_j^*, n_k^*} = 0$$

$$\left. \frac{\partial f}{\partial n_{21}} \right| = 0$$

$$\left. \frac{\partial L}{\partial n_{21}} \right| = 0$$

$$\Rightarrow \left[ \left. \frac{\partial f}{\partial n_r} \right|_{\{n_i^*\}} = 0 \quad r = 1, 2, \dots \right] \quad \{n_i^*\} = \{n_1^*, n_2^*, n_3^*, \dots, n_M^*\}$$

~~$$\text{or } \frac{\partial}{\partial n_r} [\ln n_r - 1] + \beta [E_r] + \alpha = 0$$~~

$$\text{or } (2.1) \quad \left[ \begin{aligned} -[\ln n_r^* + 1] - \beta [E_r] - \alpha &= 0 \\ r &= 1, 2, 3, \dots, M \end{aligned} \right]$$

$$d) \therefore \Rightarrow \ln n_r^* = -(1 + \alpha) - \beta E_r$$

$$e) \therefore \left[ \begin{aligned} n_r^* &= C \exp[-\beta E_r] \\ r &= 1, 2, \dots, M \end{aligned} \right] \quad (2.2)$$

f) First get C:

$$\begin{aligned} \sum n_r^* &= \tilde{N} = C \sum \exp(-\beta E_r) \\ \Rightarrow C &= \frac{\tilde{N}}{\sum \exp(-\beta E_r)} \end{aligned}$$

g)

$\Rightarrow$  h) so, The probability of observing our system in (eigen-) energy state  $E_r$  is

$$P_r = \frac{n_r^*}{\tilde{N}} = \frac{\exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)} \quad (3.1)$$

i) The unknown Lagrange multiplier (which Patricia and everybody labels using the suggestive  $\beta$  is gotten using 2nd constraint:

$$\sum_r n_r^* E_r = \tilde{E}$$

$$\text{or} \quad \sum_r \frac{n_r^*}{\tilde{N}} E_r = \frac{\tilde{E}}{\tilde{N}} \equiv U$$

$$\text{or} \quad U = \frac{\sum_r E_r \exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)} \quad (3.2a)$$

$$\text{or} \quad U = - \frac{\partial}{\partial \beta} \ln \left( \sum_r \exp[-\beta E_r] \right) \quad (3.2b)$$

III) Follow Pathria to connect  
microscale to macroscale --  
via some math trickery

A)  $A \equiv U - TS$

$\Rightarrow dA = dU - Tds - sdT$

$= Tds - PdV + \mu dN - Tds - sdT$

$\boxed{dA = -PdV - sdT + \mu dN} \quad (4.1)$

B)  $\therefore (4.1) \Rightarrow$

$$\boxed{\begin{aligned} P &= - \frac{\partial A}{\partial V} \bigg|_{T, N} \\ S &= - \frac{\partial A}{\partial T} \bigg|_{V, N} \\ \mu &= \frac{\partial A}{\partial N} \bigg|_{T, V} \end{aligned}} \quad (4.2)$$

C) NOW THE TRICKERY:

$U = A + TS$

$= A + T \frac{\partial A}{\partial T} \bigg|_{V, N}$

$= -T^2 \frac{\partial (A/T)}{\partial T} \bigg|_{V, N} = \frac{\partial (A/T)}{\partial (1/T)} \leftarrow \text{proved next pg}$

$$\frac{\partial (A/T)}{\partial (1/T)} = \frac{\partial (uA)}{\partial u} = A + \frac{\partial A}{\partial u}$$

$$i) \frac{d}{dT} (1/T) = -\frac{1}{T^2} \quad (-1/T^2)$$

$$ii) \Rightarrow d(1/T) = -dT/T^2 \Rightarrow \frac{d(1/T)}{dT} = \frac{\partial(1/T)}{\partial T} \Rightarrow$$

$$\boxed{\frac{\partial(1/T)}{\partial T} = (-1/T^2)}$$

$$iii) \frac{\partial(A/T)}{\partial T} = \frac{\partial(A/T)}{\partial(1/T)} \frac{\partial(1/T)}{\partial T} = -\frac{1}{T^2} \frac{\partial(A/T)}{\partial(1/T)}$$

$$\therefore iv) \quad \boxed{\frac{\partial(A/T)}{\partial(1/T)} \Big|_{v,N} = -T^2 \frac{\partial(A/T)}{\partial T} \Big|_{v,N} = A - T \frac{\partial A}{\partial T} \Big|_{v,N} = U}$$

$\therefore v)$  compare (5.1) w/ (3.2b):

$$(5.2) \quad \boxed{U = \frac{\partial(A/T)}{\partial(1/T)} \Big|_{v,N} = -\frac{\partial \ln \left[ \sum_r \exp(-\beta E_r) \right]}{\partial \beta} \quad (3.2b)}$$

(5.1)

(+) we can't go w/ just

$\beta = 1/T$  since then

$\beta E_r$  would not be dimensionless

(+) so,  $\beta = 1/(k_B T)$  where

$k_B$  has units of  $J/K$  AND

where  $k_B$  will turn out

To be Boltzmann's constant,  $k = k_B$ .

(4) ALSO, FROM (5.2) CHOOSE

$$A/T = -k_B \ln \left( \sum_r \exp(-\beta E_r) \right)$$

or

(where we  
used  $\beta = \frac{1}{k_B T}$ )

$$\frac{A}{k_B T} = -\ln \left( \sum_r \exp(\beta E_r) \right) \quad (6.1)$$

(6.1) is the equivalent  
to  $S = k \ln \Omega$  - which,  
it turns out - applies  
to a microcanonical  
ensemble  $\equiv$  an ensemble in  
which

IV) A Few more macroscale  
THERMO RELATIONSHIPS (follow  
PATHRIA Sec. 3.3)

a)  $C_V \equiv \left. \frac{\partial U}{\partial T} \right|_{N,V} = \left. \frac{\partial}{\partial T} \left( A - T \left( \frac{\partial A}{\partial T} \right)_{N,V} \right) \right|_{N,V}$

$$dC_v = \frac{\partial H}{\partial T}|_{N,V} - \frac{\partial A}{\partial T}|_{N,V} - T \frac{\partial^2 A}{\partial T^2}|_{N,V}$$

$$C_v = -T \frac{\partial^2 A}{\partial T^2}|_{N,V}$$

b)  $P$ :

$$P = - \frac{\partial A}{\partial V}|_{N,T} \quad \text{pg. (C\&1)}$$

$$= - \frac{\partial}{\partial V} \left[ \frac{1}{T} \ln \left[ \sum_r \exp(-\beta E_r) \right] \right] \bigg|_{N,T}$$

$$= - \frac{1}{T} \frac{\sum_r E_r \frac{\partial E_r}{\partial V} e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

$$P = - \frac{\sum_r \left( \frac{\partial E_r}{\partial V} \right) e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = - \sum_r p_r \frac{\partial E_r}{\partial V} \bigg|_{N,T} \quad (7.1)$$

where  $Q_N \equiv \sum_r \exp[-\beta E_r] = Q_N(N, V, T)$

c) For a fixed  $N$  <sup>SKIP</sup> differentiate) microscopic process, the  
1st law ( $du =$

c)  $\therefore \left( \frac{d}{dt} \right) P_{\text{tot}} = - \sum_i P_i \frac{dE_i}{dt} = - \sum_i P_i \frac{dE_i}{dt} = - \sum_i P_i dE_i$

\* BUT,  $\sum P_i dE_i$  we can interpret as  $dU$ .  
\* since  $dU = d\left(\sum_i P_i E_i\right)$

$$= \sum_i P_i dE_i$$

$\therefore \text{Eq. (1)} \Rightarrow \boxed{P_{\text{tot}} = - \sum_i P_i dE_i = -dU}$

\* AGAIN:  $\sum_i P_i dE_i = \sum_i P_i [E_{i, \text{final}} - E_{i, \text{initial}}]$   
 $= \sum_i P_i E_{i, \text{final}} - \sum_i P_i E_{i, \text{initial}}$   
 $= U_{\text{final}} - U_{\text{initial}}$   
IF  $P_i$ 's ~~don't~~ don't change during Pdt process

BOTH OF THE ABOVE ARGUMENTS  
 (that  $\sum P_i dE_i = dU$ ) ARE  
WORK -- NOW TO KEEP COOKING